3506 *J. Am. Chem. Soc.* **1998,** *120,* 3506−3507

Synthesis of Titanium Cyclynes $Cp_2Ti(OBET)$ and $Cp^*{}_2Ti(OBET)$ and the Unusual Stability of the Bimetallic Complex $Ni[Cp_2Ti(OBET)]$ to CO and O_2

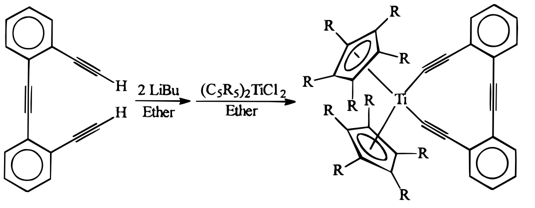
Daming Zhang, David B. McConville, Joseph M. Hrabusa, III,
Claire A. Tessier,* and Wiley J. Youngs*

Department of Chemistry, The University of Akron
Akron, Ohio 44325-3601

Received September 30, 1997

Titanocene acetylide complexes[1] have drawn considerable attention in regards to their third-order nonlinear optical properties,[2] the preparation of very hard and thermally stable metal carbides,[3] and the preparation of bimetallic tweezer complexes.[4] Tweezer complexes have been studied with the goal of understanding metal−ligand interactions, metal−metal interactions, and metal−metal cooperation in catalytically activated molecular substrates. The recent interest in titanium acetylide tweezer complexes coupled with our success in preparing platinum[5] and group 14 element[6] derivatives of the ligand *o*-bis(ethynyl)tolane (OBET, see eq 1) and their metal complexes have stimulated us to prepare the first titanium complexes of a cyclic acetylide: $Cp_2Ti(OBET)$, $Cp^*{}_2Ti(OBET)$, and the bimetallic complex $Ni[Cp_2Ti(OBET)]$ (Cp = cyclopentadienyl). The nickel derivative shows a very surprising lack of reactivity toward CO and O_2, especially when compared to similar group 14 compounds $Ni[R_2E(OBET))]$ (E = Si and Ge).

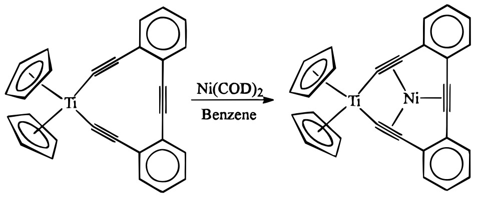
The syntheses of $Cp_2Ti(OBET)$ and $Cp^*{}_2Ti(OBET))$ are shown in eq 1. Reaction of 2,2′-diethynyltolane $[(OBET)H_2]$ with *n*-BuLi in ether results in the in situ formation of $Li_2(OBET)$. The combination of $Li_2(OBET)$ with the respective titanocene dichloride gives $Cp_2Ti(OBET)$ (24%) or $Cp^*{}_2Ti(OBET)$ (39%).[7] These two complexes can survive in air for a few hours in the solid state and a short period in solution. They are light-sensitive even in an inert atmosphere and especially in solution. The IR C≡C stretching absorptions are observed at 2069 cm^{-1} for $Cp_2Ti(OBET)$ and at 2060 cm^{-1} for $Cp^*{}_2Ti(OBET)$, and these are similar to that of $Cp_2Ti(C{\equiv}CPh)_2$ (2060 cm^{-1}).[8] The ^1H NMR spectra of these two compounds exhibit very similar patterns. In $Cp_2Ti(OBET)$ the Cp carbons appear at 114 ppm in the ^{13}C NMR spectra, whereas the Cp carbons of $Cp^*{}_2Ti(OBET)$ appear in the same region as the aromatic carbons of OBET and have not been assigned. Large shifts for α-C and *β*-C of the acetylide in the ^{13}C NMR (161 and 133 ppm in $Cp_2Ti(OBET)$ and 169 and 132 ppm in $Cp^*{}_2Ti(OBET)$) were observed, which are consistent with those reported for other titanocene acetylide complexes.[1,4,9]



(1)

$(OBET)H_2$

R = H, $Cp_2Ti(OBET)$
R = Me, $Cp^*{}_2Ti(OBET)$



(2)

$Cp_2Ti(OBET)$

$Ni[Cp_2Ti(OBET)]$

The reaction of $Cp_2Ti(OBET)$ with $Ni(COD)_2$ in benzene results in the formation of $Ni[Cp_2Ti(OBET)]$ (eq 2).[10] The complex has a red color, which is very similar to the color of the starting compound $Cp_2Ti(OBET)$. This is very different than the

---

[1] (a) Köpf, H.; Schmidt, M. *J. Organomet. Chem.* **1967**, *10*, 383. (b) Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87.

[2] (a) Myers, L. K.; Langhoff, C.; Thompson, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 7560. (b) Myers, L. K.; Ho, D. M.; Thompson, M. E.; Langhoff, C. *Polyhedron* **1995**, *14*, 57.

[3] Lang, H.; Seyferth, D. *Appl. Organomet. Chem.* **1990**, *4*, 599.

[4] (a) Yasufuku, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2664. (b) Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5. (c) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *Ibid.* **1991**, *409*, C7. (d) Lang, H.; Imhof, W. *Chem. Ber.* **1992**, *125*, 1307. (e) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008. (f) Lang, H.; Herres, M.; Zsolnai, L. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 429. (g) Lang, H.; Herres, M.; Imhof, W. *J. Organomet. Chem.* **1994**, *465*, 283. (h) Lang, H.; Weber, C. *Organometallics* **1995**, *14*, 4415. (i) Janssen, M. D.; Herres, M.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1995**, 925. (j) Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R.; Rosenthal, U. *J. Chem. Soc., Chem. Commun.* **1995**, 1753. (k) Lang, H.; Blau, S.; Nuber, B.; Zsolnai, L. *Organometallics* **1995**, *14*, 3216. (l) Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 2476.

[5] (a) Bradshaw, J. D.; Guo, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1996**, *15*, 2582. (b) Zhang, D.; McConville, D. B.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1997**, *16*, 824.

[6] (a) Guo, L.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1995**, *14*, 586. (b) Guo, L.; Bradshaw, J. D.; McConville, D. B.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1997**, 16(8), 1685.

[7] Synthesis of $Cp_2Ti(OBET)$: $(OBET)H_2$ (0.441 g, 1.95 mmol) was dissolved in ether (30 mL), and *n*-BuLi in hexane (2.70 mL of 1.51 M, 3.90 mmol) was added to the solution via syringe. The reaction mixture was stirred at room temperature for 15 min, and then the dark red colored solution was cooled to 0 °C. A suspension of Cp_2TiCl_2 (0.486 g, 1.95 mmol) in ether (40 mL) was transferred via cannula to the cooled red solution. This reaction mixture was stirred at 0 °C for 1 h and at room temperature for 10 h. This gave a red solution and a yellow precipitate. The yellow solid was removed by filtration. The solvent was removed in vacuo, and the resulting solid residue was dried in vacuo. By washing with hexane/ether (3/1, 40 mL) a red solid was obtained. Yield: 0.190 g, 24.2%. Anal. Calcd for $C_{28}H_{18}Ti$: C, 83.58; H, 4.5. Found: C, 83.88; H, 4.78. FD-MS: *m*/*e* 402 (M^+). IR (Nujol mull): $\nu(C{\equiv}C)$ 2069 cm^{-1} (weak). UV−vis (THF): 470 (weak), 398 (weak), 284 (shoulder), 268, 254 (shoulder) nm. ^1H NMR (C_6D_6): δ 7.54 (d, 2H, $J = 7.6$ Hz), 7.48 (d, 2H, $J = 7.6$ Hz), 6.95 (t, 2H, $J = 7.66$ Hz), 6.84 (t, 2H, $J = 7.6$ Hz), 6.0 (s, 10H). ^{13}C NMR (C_6D_6): δ 160.94, 133.22, 129.43, 129.19, 128.61, 126.27, 125.09, 124.91, 114.19, 94.44. Synthesis of $Cp^*{}_2Ti(OBET)$: $Cp^*{}_2TiCl_2$ (0.191 g, 0.442 mmol) was suspended in ether (20 mL). $(OBET)H_2$ (0.1 g, 0.442 mmol) was dissolved in ether (50 mL), and *n*-BuLi in hexane (3.54 mL of 2.5 M, 0.884 mmol) was added at −40 °C via syringe. The reaction mixture was stirred at −40 to −10 °C for 1 h and then was transferred to the $Cp^*{}_2TiCl_2$/ether suspension via cannula at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at room temperature overnight. After the solid was filtered, the solvent was removed from the red colored solution in vacuo. The red solid was dried in vacuo and extracted with a mixture of hexane/ether (5/1). Solvent was removed in vacuo from the extract, and the resulting red solid was dried in vacuo. Yield: 0.09 g, 39%. FD-MS: *m*/*e* 542 (M^+). IR (Nujol mull): $\nu(C{\equiv}C)$ 2060 cm^{-1} (weak). ^1H NMR (C_6D_6): δ 7.56 (dd, 2H, $J^3 = 7.66$ Hz, $J^5 = 1.4$ Hz), 7.37 (dd, 2H, $J^3 = 7.66$ Hz, $J^5 = 1.4$ Hz), 6.98 (dt, 2H, $J^3 = 7.66$ Hz, $J^5 = 1.4$ Hz), 6.84 (dt, 2H, $J^3 = 7.66$ Hz, $J^5 = 1.4$ Hz), 1.95 (s, 30). ^{13}C NMR (C_6D_6): δ 169.67, 132.92, 130.09, 129.41, 125.58, 124.76, 124.19, 123.93, 119.87, 94.21, 13.24.

[8] Lang, H.; Seyferth, D. *Z. Naturforsch.* **1990**, *45*b, 212.

[9] Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382.

[10] Synthesis of $Ni[Cp_2Ti(OBET)]$: $Cp_2Ti(OBET)$ (0.08 g, 0.2 mmol) and $Ni(COD)_2$ (0.057 g, 0.202 mmol) were combined in benzene (30 mL). The red reaction mixture was stirred at room temperature overnight. There was no significant color change. The mixture was filtered, the solvent was removed in vacuo, and the red residue was dried in vacuo. ^1H NMR indicated a greater than 98% yield. Anal. Calcd for $C_{28}H_{18}NiTi$: C, 72.94; H, 3.94. Found: C, 72.77; H, 3.93. FD-MS: *m*/*e* 460 (M^+). IR (Nujol mull): $\nu(C{\equiv}C)$ 1982, 1904 cm^{-1} (medium). UV−vis (THF): 495 (weak), 349, 282 (shoulder), 270 nm. ^1H NMR (C_6D_6): δ 7.96 (dd, 2H, $J^3 = 6.8$ Hz, $J^5 = 2.1$ Hz), 7.82 (dd, 2H, $J^3 = 6.8$ Hz, $J^5 = 2.1$ Hz), 7.02 (m, 4H), 5.35 (s, 10H). ^{13}C NMR (C_6D_6): δ 190.18, 139.67, 135.88, 130.48, 129.33, 127.93, 125.92, 120.59, 109.66, 105.18.

S0002-7863(97)03410-0 CCC: $15.00

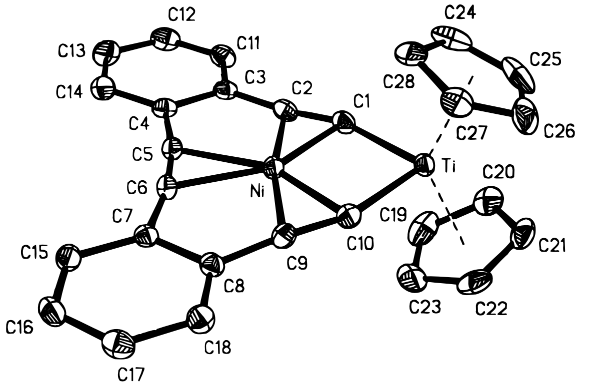


Figure 1. Structure of $Ni[Cp_2Ti(OBET)]$ with hydrogens omitted for clarity.

reactions of $R_2E(OBET)$ (E = Si, Ge) with $Ni(COD)_2$, which show a dramatic color change from colorless to deep blue. The IR C≡C stretching band appears at 2069 cm^{-1} for the free ligand $Cp_2Ti(OBET)$, whereas the C≡C stretching bands for $Ni[Cp_2Ti(OBET)]$ appear at 1982 and 1904 cm^{-1}. Similar changes in the IR spectra were observed in $R_2E(OBET)$ and $Ni[R_2E(OBET)]$ (E = Si and Ge).[6]

The ^1H NMR spectra of the nickel complex $Ni[Cp_2Ti(OBET)]$ and its free ligand $Cp_2Ti(OBET)$ exhibit similar patterns. In the nickel complex $Ni[Cp_2Ti(OBET)]$, an upfield shift of 0.65 ppm for the Cp protons relative to those in $Cp_2Ti(OBET)$ was observed, while in the ^{13}C NMR spectrum, an upfield shift of 9 ppm for the Cp carbons was observed. The alkyne carbons in $Ni[Cp_2Ti(OBET)]$ show downfield shifts in the ^{13}C NMR spectrum with the α-C of the acetylide at 190.18 ppm and the β-C at 139.67 ppm. Such shifts were also reported for $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2]$ and its nickel−monocarbonyl complex.[4d,8] In contrast, the α-C resonance shifts upfield from 96.9 ppm in $Ph_2Si(OBET)$ to 73.8 ppm in its nickel complex $Ni[Ph_2Si(OBET)]$, indicating that the coordination of Ni(0) strongly shields the alkyne carbons adjacent to the silicon with the other alkyne carbons shifting downfield.[6] In tribenzocyclyne (TBC, $R_2E(OBET)$ with R_2E = $(o)C_6H_4$), the alkyne carbon resonance shifts downfield from 93.6 ppm for the free ligand to 109.6 ppm upon coordination with nickel(0).[11] The UV−vis spectra for $Cp_2Ti(OBET)$ and $Ni[Cp_2Ti(OBET)]$ show similar features; strong bands at approximately 270 nm and significantly weaker bands at approximately 470 and 495 nm.

The structure of $Ni[Cp_2Ti(OBET)]$ has been solved by X-ray crystallography (Figure 1).[12,13] This compound crystallizes in the monoclinic space group $P2_1/n$. The pocket is planar with a root-mean-square deviation of 0.028 Å from the plane defined by C1−C10 and the Ti atom. The nickel atom is bound to three alkynes and is in the plane defined by C1−C10 and Ti atoms with a deviation of 0.003 Å. The distances from the Ni atom to C1 (2.006(2) Å), C10 (2.010(3) Å), C5 (2.005(3) Å), and C6 (2.012(2) Å) are shorter than the distances of Ni to C2 (2.044(2) Å) and C9 (2.042(2) Å). The corresponding distances in $Ni[Ph_2Si(OBET)]$ are 2.052(4) Å (Ni−C1), 2.047(5) Å (Ni−C10), 1.999(5) Å (Ni−C2), 2.005(5) Å (Ni−C9), 1.990(5) Å (Ni−C5), and 1.989(4) Å (Ni−C6) Å.[6] In $Ni[Cp_2Ti(OBET)]$, the average distance of the Ni atom to the carbon atoms of three alkynes is 2.019 Å compared with the average distance of 1.958 Å in Ni(TBC)[11] and 2.015 Å in $Ni[Ph_2Si(OBET)]$. The Ni to alkyne distances in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2\}Ni(CO)$ are 2.060 Å for the carbons α to Ti and 2.067 Å for the carbons β to Ti. The Ni−Ti distance of 2.7737(7) Å in $Ni[Cp_2Ti(OBET)]$ is significantly shorter than the Ni−Ti distance (2.882 Å) in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2\}Ni(CO)$[4d] but longer than the sum of the covalent radii for Ni and Ti. The titanium−acetylide distances (C1−Ti = 2.079(3) Å and C2−Ti = 2.070(3) Å) are slightly shorter than the equivalent bonds (2.107 Å) in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2\}Ni(CO)$. The C≡C bond distance of the acetylides (1.251(4) Å) is not significantly different than the third alkyne (1.241(4) Å) and the acetylides in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2\}Ni(CO)$ (1.233(10) Å). A "trans" geometry is observed for the acetylides. Such "trans" geometry was also observed for the acetylides in $Ni[Ph_2Si(OBET)]$.[6]

Carbon monoxide was bubbled through a solution of $Ni[Cp_2Ti(OBET)]$ in benzene for 2 h and then the flask was sealed for 1 week. The solvent was removed in vacuo, and the residue was characterized by ^1H and ^{13}C NMR. The spectra showed only the presence of $Ni[Cp_2Ti(OBET)]$. In contrast, Ni(TBC)[11] or $Ni[Ph_2Si(OBET)]$[6] gave the free the ligand TBC or $Ph_2Si(OBET)$ after CO was bubbled into the solution for only 2−5 min.[6,11] There was no rapid reaction when oxygen, or water and air, was allowed to react with a benzene solution of $Ni[Cp_2Ti(OBET)]$. In contrast, Ni(TBC) or $Ni[Ph_2Si(OBET)]$ decomposes to give the free ligand in 5 min when exposed to air.[6,11] Neither $Ni[Cp_2Ti(OBET)]$ nor Ni(TBC)[11] reacts with PMe_3. After the solution of $Ni[Cp_2Ti(OBET)]$ interacted with oxygen for 3 days or water/air overnight, NMR spectra show small peaks at 6.02 ppm (Cp-H) and 114 ppm (Cp-C) which indicate a slow decomposition. These observations indicate a much stronger bonding of the nickel atom to other atoms in $Ni[Cp_2Ti(OBET)]$ than in Ni(TBC) or $Ni[Ph_2Si(OBET)]$. There are at least two options that can be envisioned that account for the increased stability of the Ni(0) and Ti(IV) centers in $Ni[Cp_2Ti(OBET)]$. One possibility is that there is a direct Ni−Ti bond in this complex with electron donation from the Ni(0) to the Ti(IV). The other possibility involves an indirect stabilization of the Ni−alkyne bonds by the electropositive titanium. The titanium atom or the $TiCp_2$ moiety would be expected to withdraw electron density from the π^* acetylide orbitals. This, in turn, would allow the nickel atom to increase its donation to the π^* orbitals of the acetylides. The upfield shifts for the Cp protons and the Cp carbons in $Ni[Cp_2Ti(OBET)]$ relative to those in $Cp_2Ti(OBET)$ are consistent with more electron density being present on the Cp_2Ti moiety in $Ni[Cp_2Ti(OBET)]$ than in $Cp_2Ti(OBET)$. These scenarios may also apply to the Ti acetylide tweezer complexes previously reported.[4] We note that $Ni[Cp_2Ti(OBET)]$ is significantly less reactive than similar tweezer complexes; $(C_5H_4SiMe_3)_2Ti(CCPh)_2NiCO$ reacts with tertiary phosphines to give substitution of the carbon monoxide ligand.[4d] The extra stability of $Ni[Cp_2Ti(OBET)]$ with respect to tweezer complexes is probably due to the chelating nature of the OBET ligand.

We are currently synthesizing a variety of mixed early−late transition metal systems utilizing the OBET and related ligands with the goals of studying the reaction chemistry and the nonlinear optical (NLO) properties of a series of these mixed metal complexes. We are also studying the bonding in $Ni[Cp_2Ti(OBET)]$ with ab intio and semiempirical theoretical calculations.

Acknowledgment. We thank the National Science Foundation for financial support and Dr. Robert Lattimer of BFGoodrich for providing the FD-MS data.

Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9734105

---

(11) (a) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719. (b) Ferrara, J. D.; Tanaka, A. A.; Fierro, C.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2089.

(12) Crystal Data: $C_{28}H_{18}NiTi$, $M = 461.03$, monoclinic, space group $P2_1/n$, $a = 14.802(3)$ Å, $b = 8.235(2)$ Å, $c = 16.222(3)$ Å, $\beta = 96.72(2)°$, $V = 1963.8(7)$ Å^3, $Z = 4$, $\mu = 1.378$ mm^{-1}, $F(000) = 944$, $T = 172$ K. Refinement for all unique data (3449 reflections) gave $wR2(F^2) = 7.52\%$ (all data) and $R1(F) = 3.16\%$ ($I > 2\sigma(I)$) with a GOF on F^2 of 1.027.

(13) (a) *SHELXTL PLUS* V. 4.03; Siemens Analytical Instruments, Inc.: Madison, WI, 1990. (b) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.